

# Radio Frequency Plasma Synthesis of Boron Nitride Nanotubes (BNNTs) for Structural Applications: Part K

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## Abstract

It is evident that nanotubes, such as carbon, boron nitride and even silicon, offer great potential for many aerospace applications. The opportunity exists to harness the extremely high strength and stiffness exhibited by high-purity, low-defect nanotubes in structural materials. Even though the technology associated with carbon nanotube (CNT) development is mature, the mechanical property benefits have yet to be fully realized. Boron nitride nanotubes (BNNTs) offer similar structural benefits, but exhibit superior chemical and thermal stability. A broader range of potential structural applications results, particularly as reinforcing agents for metal- and ceramic-based composites. However, synthesis of BNNTs is more challenging than CNTs mainly because of the higher processing temperatures required, and mass production techniques have yet to emerge. A promising technique is radio frequency plasma spray (RFPS), which is an inductively coupled, very high temperature process. The lack of electrodes and the self-contained, inert gas environment lend themselves to an ultraclean product. It is the aim of this White Paper to survey the state of the art with regard to nano-material production by analyzing the pros and cons of existing methods. The intention is to combine the best concepts and apply the NASA Langley Research Center (LaRC) RFPS facility to reliably synthesize large quantities of consistent, high-purity BNNTs.

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## Symbols and Abbreviations

### Abbreviations

BNNT.....	boron nitride nanotube
BOCVD.....	boric oxide chemical vapor deposition
CNT.....	carbon nanotube
CVD .....	chemical vapor deposition
DC .....	direct current
DWNT.....	double-walled nanotube
h-BN.....	hexagonal boron nitride
JL.....	Jefferson Lab
LaRC .....	Langley Research Center
MWNT.....	multi-walled nanotube
NIA .....	National Institute of Aerospace
NRC-C .....	National Research Council - Canada
NT .....	nanotube
PVC.....	pressurized vapor/condenser
RF.....	radio frequency
RFPS .....	radio frequency plasma spray
slpm.....	standard liters per minute
SWNT .....	single-walled nanotube

## 1. Introduction

There has been a great deal of aggressive promotion regarding the use of nanotubes in a wide variety of applications. Indeed, the projected physical and mechanical properties are very appealing, but taking advantage of them has proved to be problematic. Among the potential applications, it is evident that using nanotubes as reinforcing agents for structural materials may be the most challenging (ref. 1). Although carbon nanotubes (CNTs) are now mass-produced, the technology surrounding CNT-reinforced composites is still in its infancy. The crystal structure and physical morphology of boron nitride nanotubes (BNNTs) are analogous to CNTs. BNNTs offer the same potential benefits as CNTs, but exhibit superior chemical and thermal stability (ref. 2). In contrast with CNTs, which are conductors, BNNTs are insulators. These combined characteristics make BNNTs more compatible with metal-matrix composites, i.e. no fiber-matrix galvanic interactions and much higher temperature application. An additional benefit of BNNT-reinforced composites is that a boron-containing structural material may also provide protection against certain types of radiation (ref. 3). However, such real-world applications will only emerge if commercial quantities of high-quality BNNTs are available to the aerospace industry.

In the case of CNTs, the production of single-walled (SWNTs), double-walled (DWNTs), or multi-walled (MWNTs) nanotubes represents a mature technology. In contrast, the high temperatures and chemical reactions associated with synthesis of BNNTs have severely restricted the quality and quantity of products available (ref. 2). The best nanotubes have been formed when synthesis is conducted above the vaporization point of boron ( $T \sim 4000^{\circ}\text{C}$ ). Incumbent manufacturing techniques tend to be slow because they are batch-style processes which employ consumable electrodes or targets (ref. 4). The application of radio frequency plasma spray (RFPS) technology may be an attractive alternative for cost-effective synthesis of high-purity, low-defect BNNTs (ref. 5). The electrodeless, inductively-coupled process offers very high temperatures ( $T > 10,000^{\circ}\text{C}$ ) in an inert, low-pressure environment (fig. 1a). This rapid, semi-continuous processing capability is available at the Langley Research Center (LaRC), and the RFPS facility represents an opportunity to investigate mass production of high quality BNNTs (fig. 1b). The purpose of this paper is to provide a survey of the incumbent BNNT synthesis techniques, and identify processing concepts and methodologies applicable to the proposed LaRC effort.

BNNTs are a structural analog of CNTs, replacing C atom pairs with alternating B and N atoms in a tubular structure (fig. 2) (ref. 6). The three principal crystal structures associated with SWNTs are shown in figure 2a, and the relative dimensions of SWNTs, DWNTs, and MWNTs are illustrated in figure 2b, colored blue, green and red, respectively (ref. 7). Processing studies have established that the crystal structure and morphology (number of concentric shells) are dependent on the synthesis method employed (ref. 3). In any manifestation, BNNTs offer the highest potential as reinforcing agents for metal matrices, providing that the product is high-purity and defect-free. Based on specific properties, SWNTs are stronger by weight, and MWNTs are stronger by volume (ref. 1). This suggests that synthesis of small-diameter SWNTs for aerospace composite/hybrid materials, in which weight is critical, may be an appropriate target for future development.

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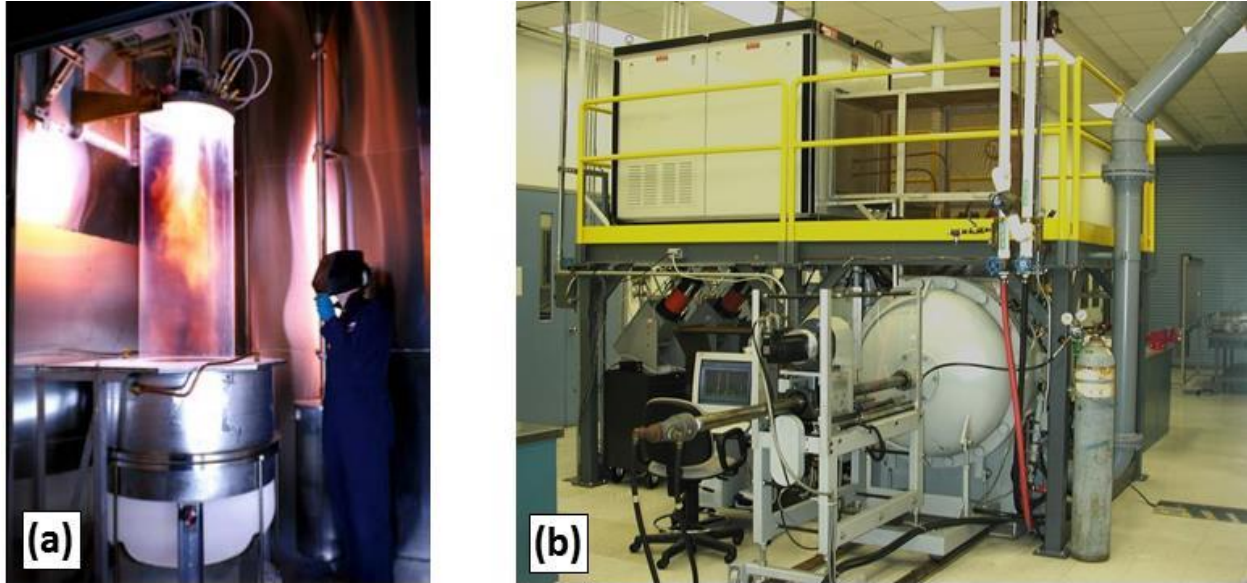


Figure 1. Radio frequency plasma synthesis; (a) Inductively-coupled plasma generated by high-frequency discharge (ref. 5); (b) NASA LaRC RF plasma spray facility.

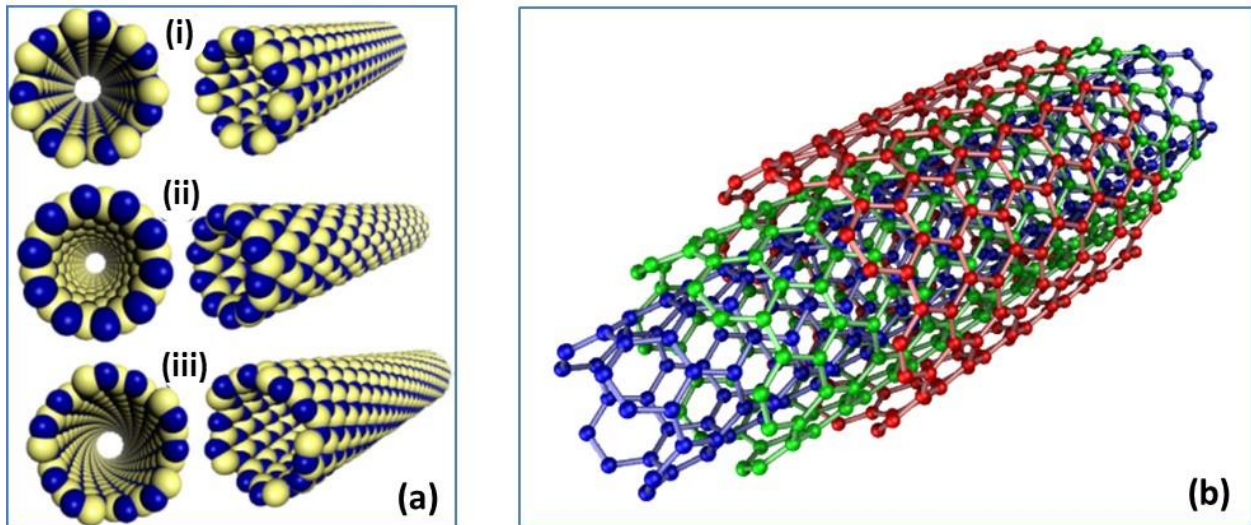


Figure 2. Nanotube architecture: (a), Types of single-walled BNNTs; (i) arm-chair (10,10), (ii) zig-zag (20,0), (iii) chiral (10,3) (ref. 6); and (b), Relative diameters of single- [blue], double- [green], and multi-walled [red] NTs (ref. 7).

Regardless of nanotube diameter, a preliminary assessment of the use of BNNTs as structural reinforcement of metal-matrix composites reveals some important considerations:

- Improved thermal oxidative stability of BNNT versus CNT
  - In contrast with CNTs, which have a maximum use temperature of  $\sim 500^{\circ}\text{C}$ , in the presence of oxygen, BNNTs are stable to  $\sim 1000^{\circ}\text{C}$  (ref. 8). Consequently, CNTs

will likely be restricted to polymer-matrix composite applications, whereas BNNTs are also thermally compatible with metal- and ceramic-matrix composites. Fiber/matrix reactions and the use of fiber barrier coatings to mitigate such reactions may still be warranted in structural material applications.

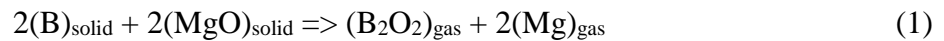
- Adhesion at the fiber-matrix interface
  - As with any fiber-reinforced material, the physical characteristics of the interface will exert a strong influence on the mechanical properties of the composite. Like carbon fibers, brittle carbide phases can form on CNTs during elevated temperature exposure (ref. 9). CNTs are electrically conductive and intimate contact with metals results in the creation of a galvanic couple, and accelerated corrosion ensues. BNNTs are chemically inert dielectric materials, so both of these issues are avoided.
- Fiber-matrix contact area
  - Experience with discontinuous reinforcement of composites suggests that, for the same volume fraction, fiber dimensions are critical, i.e. length:diameter ratio (ref. 10). A high-aspect ratio, approaching  $10^4$ , is necessary for the mechanical properties of a discontinuous-reinforced composite to be commensurate with those of its continuous-reinforced counterpart. It follows that BNNTs ~10 nm in diameter must be ~100  $\mu\text{m}$  long in order for the mechanical properties of the reinforcing agents to be fully conveyed to the metal matrix.
- Fiber fraction and distribution
  - Dispersion of BNNTs within a metal matrix will be an important element in harnessing the mechanical properties (ref. 11). As with traditional reinforcing agents, homogeneous mixing and alignment of the fibers in the appropriate volume fraction will be critical. Discontinuous-reinforced composites, with randomly-oriented strands, might be a realistic, intermediate goal for the application of BNNTs in structures.

Historically, the production of very limited quantities has hindered evaluation of the mechanical properties of BNNTs as reinforcing agents for structural materials. A recurrent issue is that the synthesis of SWNTs requires processing temperatures in excess of  $3000^\circ\text{C}$  and low pressures (ref. 12). The formation of BNNTs was only predicted in 1994, initial synthesis of MWNTs by arc discharge occurred in 1995, and refinement of the method resulted in the production of DWNTs and SWNTs in 1996 (ref. 13). In recent years, the yield of MWNTs has reached the grams level, but the mass production of high-purity, low-defect SWNTs remains a challenge. Previous work suggests that nanotube diameter will govern the strength and stiffness of BNNT-reinforced composites (ref. 14). Fewer walls or shells translates to a higher nanotube aspect ratio, which will be critical for capitalizing on the exceptional properties in bulk product. It is evident that the efficient synthesis of large quantities will be necessary for BNNTs to be utilized in large structures.

## 2. Candidates for Processing of BNNTs

### 2.1. Incumbent Synthesis Techniques

Initial BNNT synthesis methods were adapted from CNT equivalents, but dedicated methods have been developed. A variety of synthesis techniques have been successfully employed, including chemical vapor deposition (CVD), reactive ball milling, laser ablation, and arc discharge (refs. 2 and 3). The lower-temperature methods, such as CVD and ball milling, tend to result in larger quantities than high-temperature methods, but MWNTs dominate and the impurity/defect levels are high. A leading candidate among the low-temperature synthesis techniques is the boric oxide chemical vapor deposition (BOCVD) method (ref. 15). BOCVD is capable of synthesizing well-crystallized MWNTs of high purity. BNNT growth occurs within an induction furnace with a large temperature gradient (fig. 3). An equi-molar mixture of B and MgO is evaporated to produce  $B_2O_2$  gas and Mg vapor, the latter acting as a floating zone catalyst. These precursors are then transported with an Ar carrier gas into a reaction chamber fabricated from boron nitride (BN). Introducing ammonia gas ( $NH_3$ ) results in the formation and deposition of BNNTs on the wall of the chamber. The conversion rate from B to BN is approximately 40% using this processing route. The synthesis reactions which occur involve equations of the following form:



and

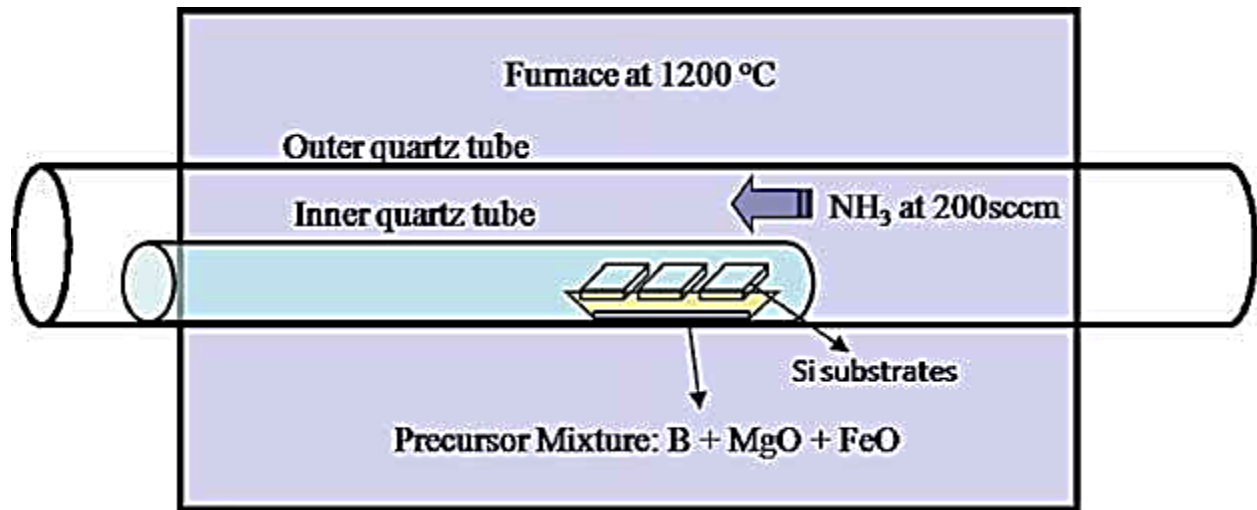
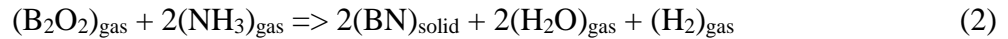


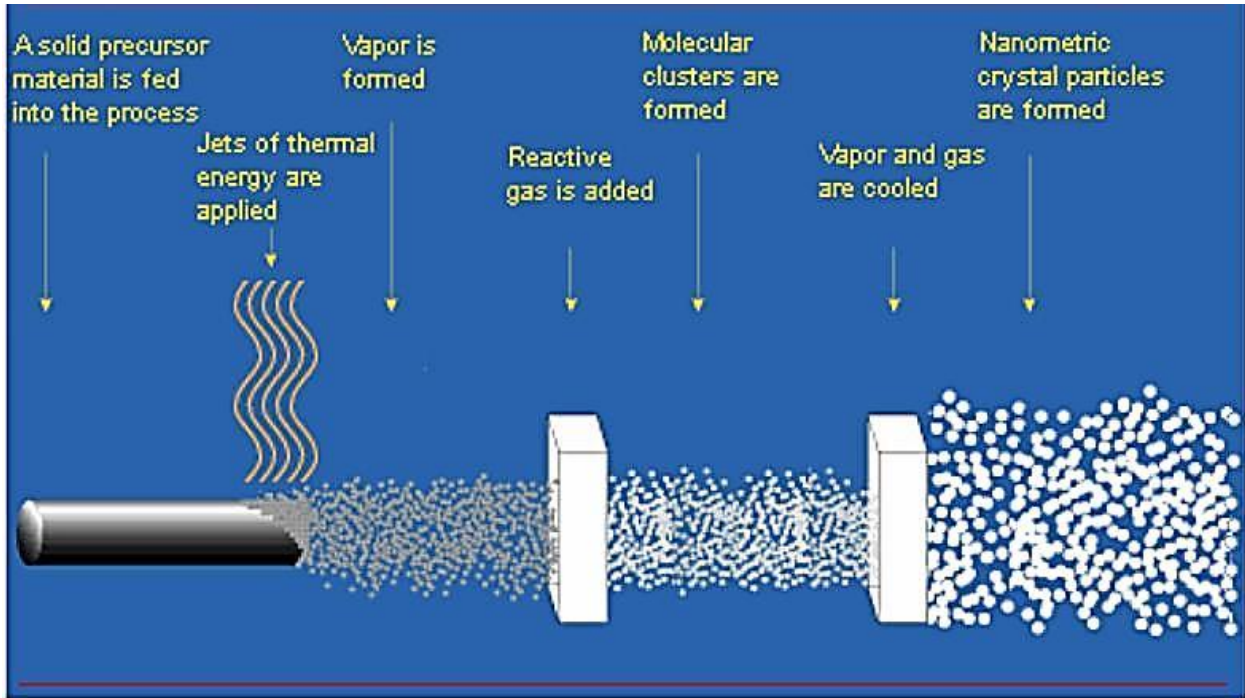
Figure 3. BOCVD method for synthesizing BNNTs (ref. 12).

BNNTs synthesized via this route tend to possess relatively large diameters of ~50–80 nm, and current efforts aim to reduce nanotube diameters to the sub-10 nm scale (ref. 4). Other shortcomings of this approach are that the reagents can be dangerous, and the deposited product



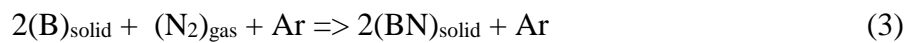
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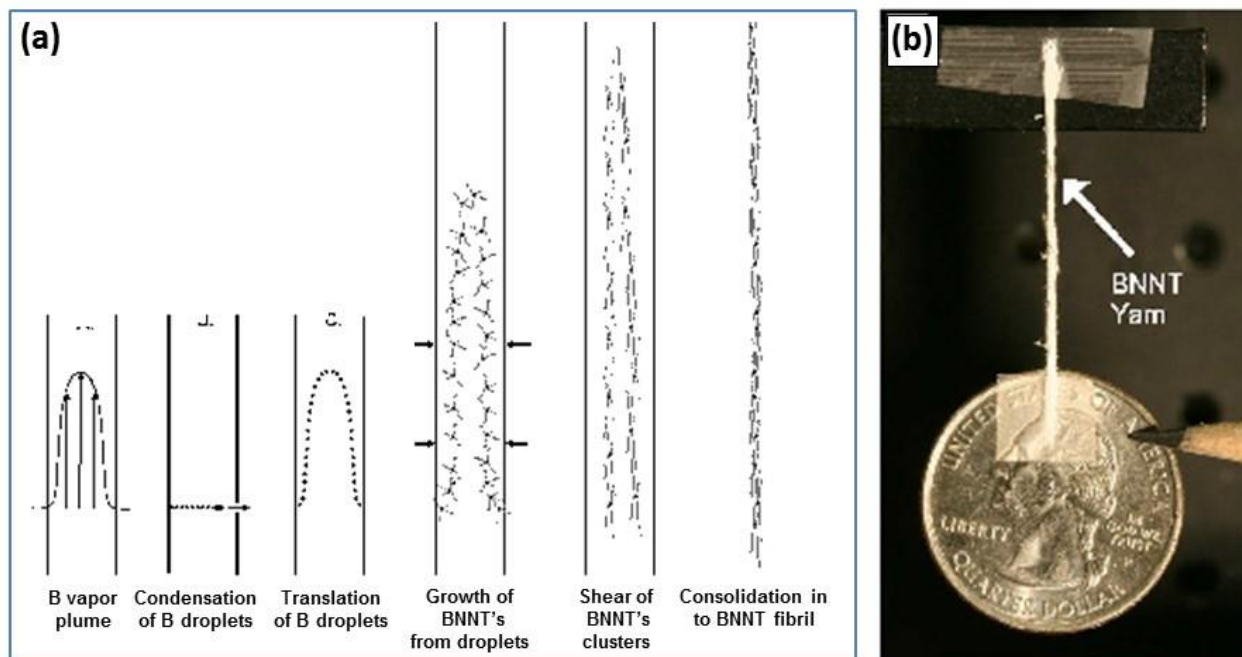
is full of defects, e.g. regions of crystallographic disorder. It transpires that high-temperature synthesis techniques may be the best candidates for high-quality SWNT production. Methods such as laser ablation and arc discharge do produce low-defect BNNTs, but in relatively small quantities. Figure 4 outlines the fundamental aspects of high-temperature processing methods used to generate large fractions of SWNTs (ref. 16). A solid precursor, often a consumable cathode, is vaporized and combined with reactive gases. The final product emerges during controlled cooling in the presence of a catalyst.



**Figure 4. Concept behind most high-temperature processing methods (ref. 16).**

A promising technique which employs this concept is referred to as the pressurized vapor/condenser (PVC) method (ref. 17). This modified laser ablation approach has been championed in a combined effort involving Jefferson Lab, the National Institute of Aerospace, and NASA LaRC (JL/NIA/LaRC). Essentially, a 5 kW-class CO<sub>2</sub> laser is used to progressively evaporate a boron target inside a vertically mounted chamber. This produces an upward stream of hot boron vapor (~4000 °C) in a high-pressure atmosphere (~1 MPa) of nitrogen gas. A wire traversing the stream of gas acts as a physical catalyst for the ensuing reaction. Condensation of the boron vapor forms liquid boron droplets which serve as nucleation sites for the growth of BNNT networks that interlock to form fibrils (fig. 5a). The typical output is ~1 mm diameter by 3 cm long yarns comprised of highly crystalline, small-diameter BNNTs (fig. 5b). In addition to the limited quantities produced (~40 mg/hr), a major limitation is that purity is still an issue as the yarns contain significant amounts of amorphous and other BN phases (ref. 2). The synthesis reaction which occurs involves an equation of the following form:





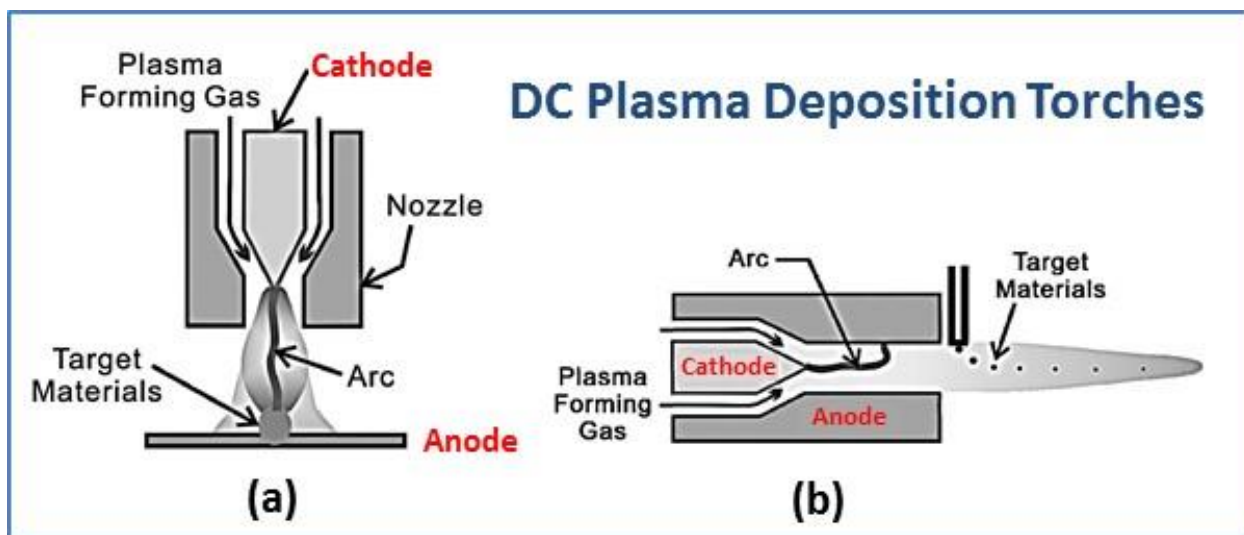
**Figure 5. Pressurized vapor/condenser method; (a) Schematic of JL/NIA/LaRC PVC technique for synthesizing BNNTs; (b) Typical BNNT yarn produced using the PVC approach (ref. 17).**

Although the PVC method is compatible with mass production of BNNTs, the use of a consumable target restricts production to batch processing. Another promising high-temperature method is arc discharge or thermal plasma processing, which avoids the use of consumable targets (ref. 3). However, the most common techniques still use consumable electrodes to generate the plasma (also a potential source of contamination). Typically, the approach involves vaporization of solid or liquid suspension precursors in a hot, ionized gas and the subsequent condensation of nano-sized particulates (ref. 16). Traditionally, the plasma-forming gas is inert, solely provides the heat source, and does not contribute to the composition of the sprayed product. In contrast, the injection of a reactive gas or liquid can be used to create *in-situ* chemical reactions with solids in the plasma plume. This approach is known as plasma-chemical processing, and is used to produce large quantities of a wide variety of nano-materials (ref. 18).

## 2.2. Direct Current (DC) Plasma Synthesis

Among arc discharge techniques, the DC thermal plasma process is most commonly applied to nano-material production. Essentially, an arc between two highly charged electrodes creates a hot ionized gas plume and the cathode is steadily consumed. In the direct method, the nozzle is neutral and the target is the anode. In the non-direct method, the nozzle becomes the annular anode (fig. 6) (ref. 20). [Traditionally, both processes are conducted under ambient conditions, and nano-material synthesis takes advantage of the inert gas shroud typically created.] Classified as high-velocity, low-volume techniques, high-purity CNTs have been synthesized via either process using carbon electrodes/targets (ref. 18). Experience shows that the yield is much higher via the non-direct approach because it represents a departure from batch processing.

Significantly, consumable electrode plasma techniques do not lend themselves readily to the synthesis of BNNTs. Electrodes made from either B or BN do not possess sufficient electrical conductivity to support an arc unless doped (or sheathed) with metals (ref. 2). Consequently, significant amounts of metallic impurities are transferred to the final product. This has led researchers to explore alternative plasma synthesis methods for the production of BNNTs. Slave BN rods have been evaporated indirectly during arc discharge processing, but the use of refined feedstock has proved to be more efficient (ref. 12). These precursors are typically transported to the reaction zone in fluid form (gas or liquid). What follows are examples of DC plasma methods employing different types of feedstock, and the precursors being injected at varying locations.



**Figure 6. DC plasma process with reaction occurring outside the discharge zone; (a) Transferred arc torch, using solid precursors as the target; (b) Non-transferred arc torch, using radial injection of solid precursors (ref. 20).**

Basic DC non-transferred arc systems operate under atmospheric pressure and involve the injection of plasma forming gases circumferentially around a consumable cathode with additional reactants being introduced outside the discharge zone (fig. 6b) (ref. 20). Such systems have been modified to incorporate the injection of additional liquid precursors radially through the anode, i.e. inside the discharge zone (fig. 7) (ref. 21). This approach also allows atomized liquid compounds or particle/liquid suspensions to be introduced into the plasma. Other systems have been modified for the injection of solid precursors radially through the anode (fig. 8) (ref. 22). This permits powders transported by a carrier gas or liquid to be introduced directly into the discharge zone.



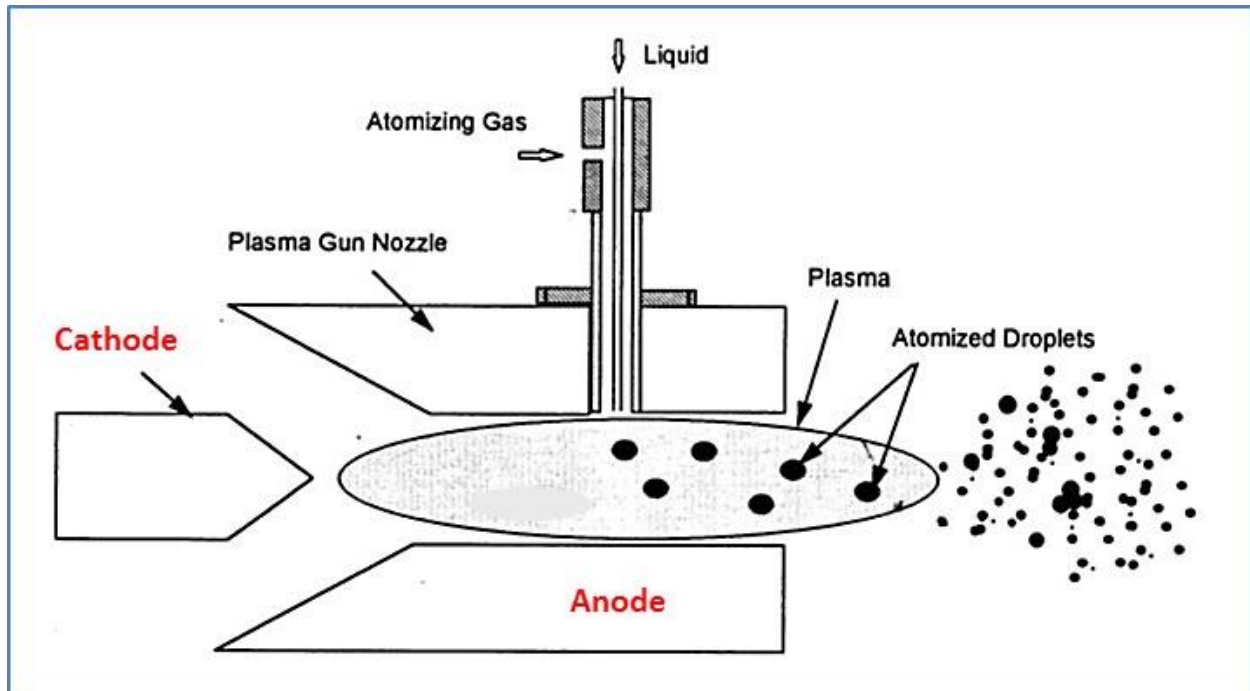


Figure 7. DC plasma process using radial injection of liquid precursors, and reaction occurring inside the discharge zone (ref. 21).

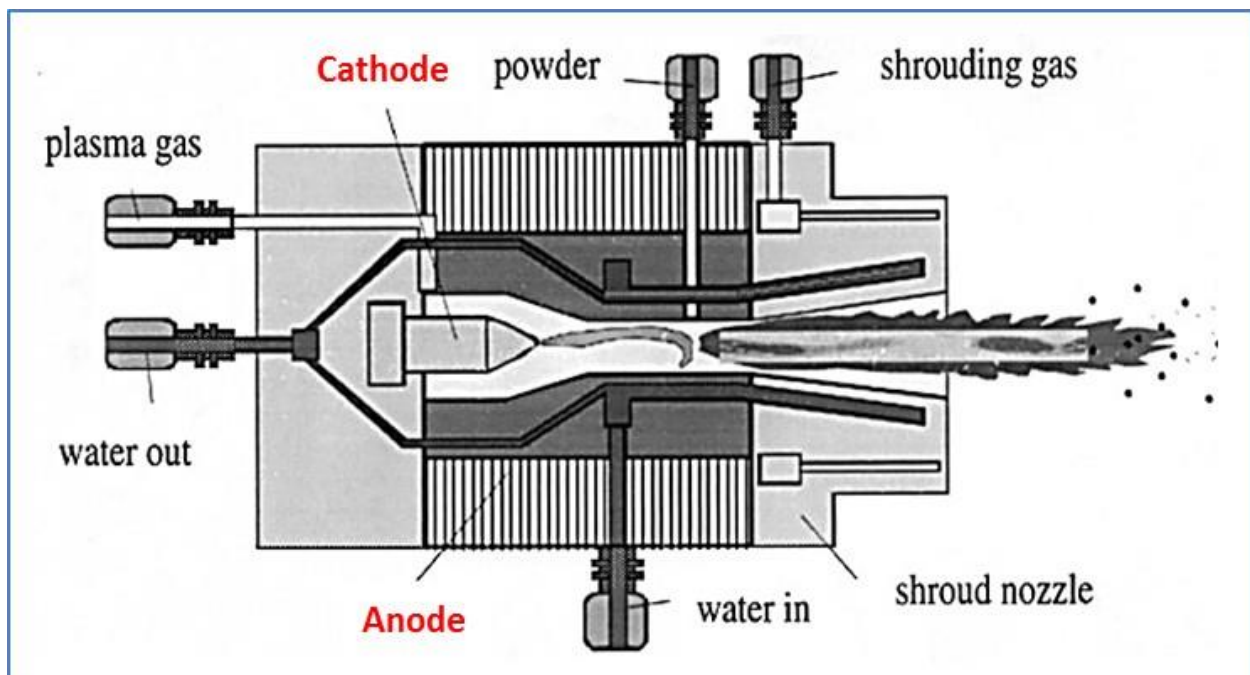


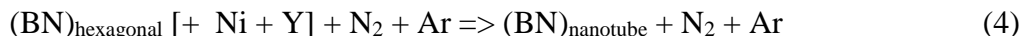
Figure 8. DC plasma process using radial injection of solid precursors, and reaction occurring inside the discharge zone (ref. 22).

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Thermal decomposition of powder feedstock starts from the powder surface and then propagates toward the powder interiors when using arc discharge or thermal plasma techniques (ref. 21). If the residence time in the high-temperature zone is not sufficient, the central regions of the particles are only partially processed. Partial conversion of particles can result in the break-up of the crystals and the formation of micro-crystals and amorphous phases. The dwell time in the plasma plume has been extended by attaching so-called “reaction chambers” to the exit nozzle of the plasma gun (ref. 18). Expanding the hot zone allows the desired transformations, conversions or chemical reactions to reach completion.

In figures 7 and 8, the precursors are injected at the location of plasma formation and chemical reactions occur inside the discharge zone. However, figure 6 indicates that some of the reactants can be introduced at the exit nozzle or beyond, such that synthesis occurs outside the discharge zone. The plasma forming gas, which is typically inert, is introduced separately and only provides the initial heat source. The subsequent injection of reactive solid, liquid, or gaseous precursors leads to less fouling of the arc chamber (ref. 24). Increased flexibility and careful control of cooling rates are benefits of this approach.

Figure 9 shows an early example of the application of the “outside the discharge zone” concept to the production of BNNTs (ref. 18). The non-transferred DC plasma process is contained within a reactor vessel operating at atmospheric pressure (ref. 25). A tungsten (W) cathode and annular copper (Cu) anode create the plasma arc using an Ar/N<sub>2</sub> mixture as the forming gas. The Ar and N<sub>2</sub> flow rates are 45 standard liters per minute (slpm) and 2 slpm, respectively. When ionized, the atomic nitrogen becomes the reactive precursor, which combines with the solid precursor injected radially at the torch exit nozzle. The synthesis reaction involved in this processing route utilizes an equation of the following form:



The reactants consist of 1 μm BN powder mixed with Ni/Y powders (atomic ratio 9:1) as catalysts. The reactant mixture is introduced into the formed plasma using Ar carrier gas at the carbon cylinder adjacent to the nozzle exit. The remaining stack of carbon cylinders serve to extend the hot zone to enhance the reaction. The end product comprises a gray deposit on the reaction chamber walls that contains BNNTs. This method is appealing because synthesis is based on a simple physical transformation of BN, the allotropic transition occurring in the presence of excessive nitrogen gas. Also, the length of the hot zone can be adjusted by choosing the number of reaction cylinders attached (ref. 25). The deficiencies of this approach are that the product has to be forcibly removed, the catalysts become impurities, and contamination will result from erosion of the W and Cu electrodes.

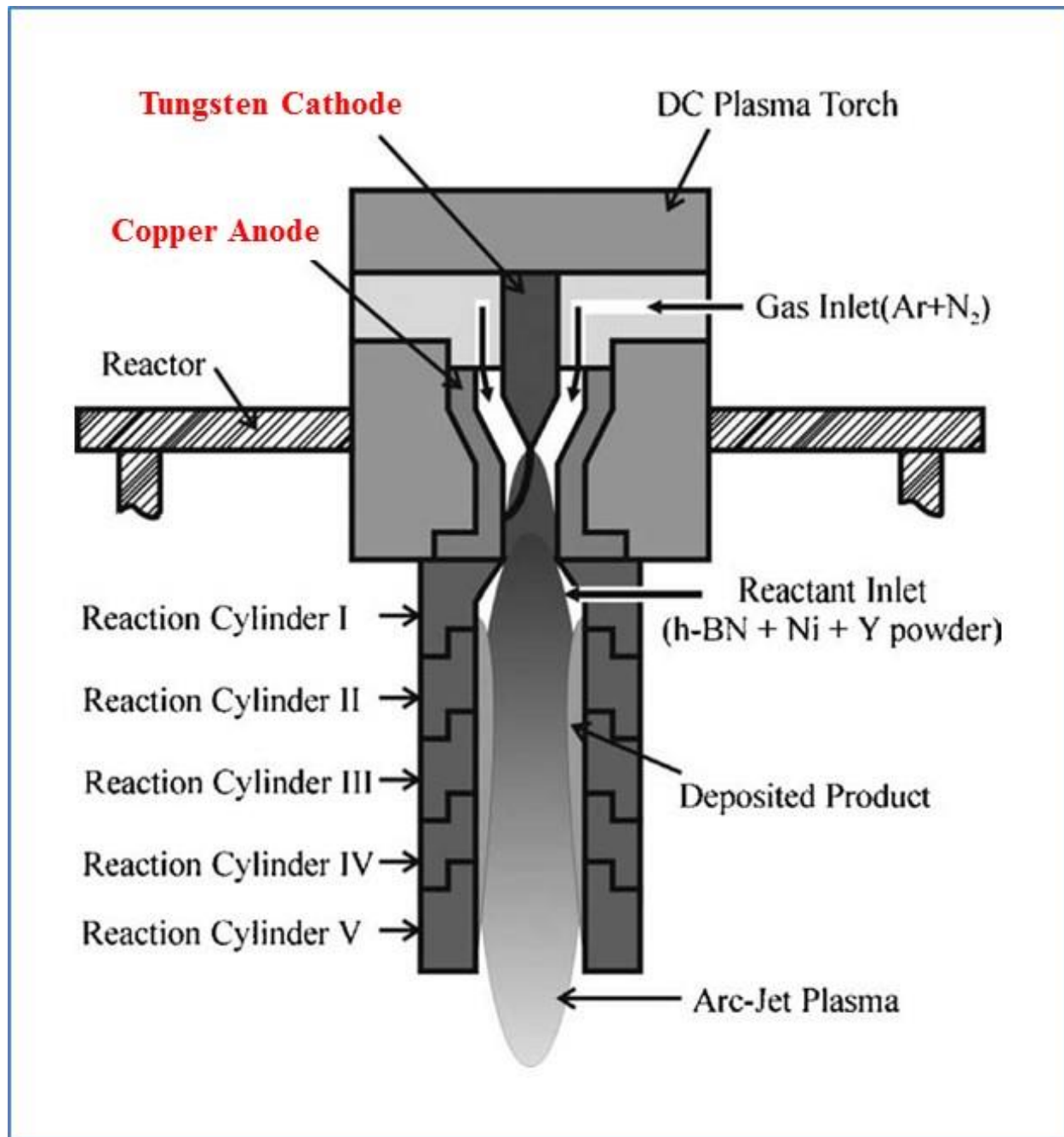


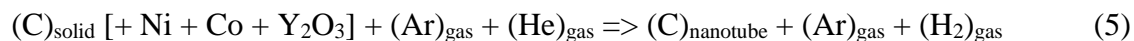
Figure 9. DC plasma process using radial injection of solid precursors, and reaction occurring outside the discharge zone (refs. 18, and 25).

### 2.3. RF Thermal Plasma Synthesis

When using DC plasma methods, the final product always suffers from the metallic impurities introduced by a consumable cathode. However, the semi-continuous nature of the process does offer hope for mass production which has lead researchers to investigate RF plasma methods. This thermal plasma technique is an electrodeless process, which uses inductive coupling to ionize an inert gas (ref. 19). Processing is conducted within an ultra-clean vessel, operating under a partial-pressure, inert gas atmosphere. In contrast with DC plasma techniques, it is classified as a low-velocity, high-volume technique and is free from contamination resulting from cathode erosion. In RF plasma torches, gaseous, liquid, or solid precursors can be injected axially, as opposed to radial injection in DC plasma torches (fig. 10). A carrier gas transports the precursors down an injection probe, which introduces the reactants in the middle of the plasma. On the Tekna RF torch shown, the central gas forms the plasma and the cooler sheath gas protects the confinement tubes. The characteristically high temperatures extending along the torch centerline permit evaporation of even the highest boiling point materials (ref. 26). The rate of chemical reaction is also enhanced by the long residence time in the very hot zone (ref. 20). The process is already being used for the synthesis of large quantities of high-purity, highly-crystalline product using a variety of precursors (ref. 5).

Tekna Plasma Systems, Inc. (Sherbrooke, Quebec, Canada) is the industry leader in RF plasma torch design/manufacture, and is also an industry leader in the commercial production of nano-powders via induction plasma synthesis (fig. 11) (ref. 5). The lack of consumable electrodes or targets allows for continuous, rather than batch, processing. The commercial scale of the operation is evident in figure 11a. The 400 kW installation produces 20–40 kg/h, depending on the nature of the feedstock and the degree of spheroidization required. The equipment set-up shown in figure 11b illustrates the self-contained nature of the process (ref. 51). The schematic in figure 11c outlines the processing details and shows the three collection points for progressively finer powder (at the bottom) (ref. 27). The typical operating parameters shown in figure 11d reveal the 5:1 ratio between sheath and central gas for effective confinement of the plasma plume.

It is important to note that Tekna currently produces nano-materials, which do not include NTs. However, the production concepts are directly applicable to the synthesis of large quantities of high-purity BNNTs. Tekna continues to evolve RF gun manufacturing and holds patents for a broad range of RF plasma processing technologies, including product collection and separation devices (ref. 19). Recently, RF technology championed by Tekna has produced significant quantities of CNTs at the University of Sherbrooke, Canada (ref. 29). The very high temperatures inherent to the process promote the allotropic transformation of carbon black powder into SWNTs using an Ar/He plasma in the presence of a mixture of metallic catalysts. The synthesis reaction involved in this processing route involves an equation of the following form:



Radio Frequency Plasma Synthesis of Boron Nitride Nanotubes (BNNTs) for Structural Applications: Part I

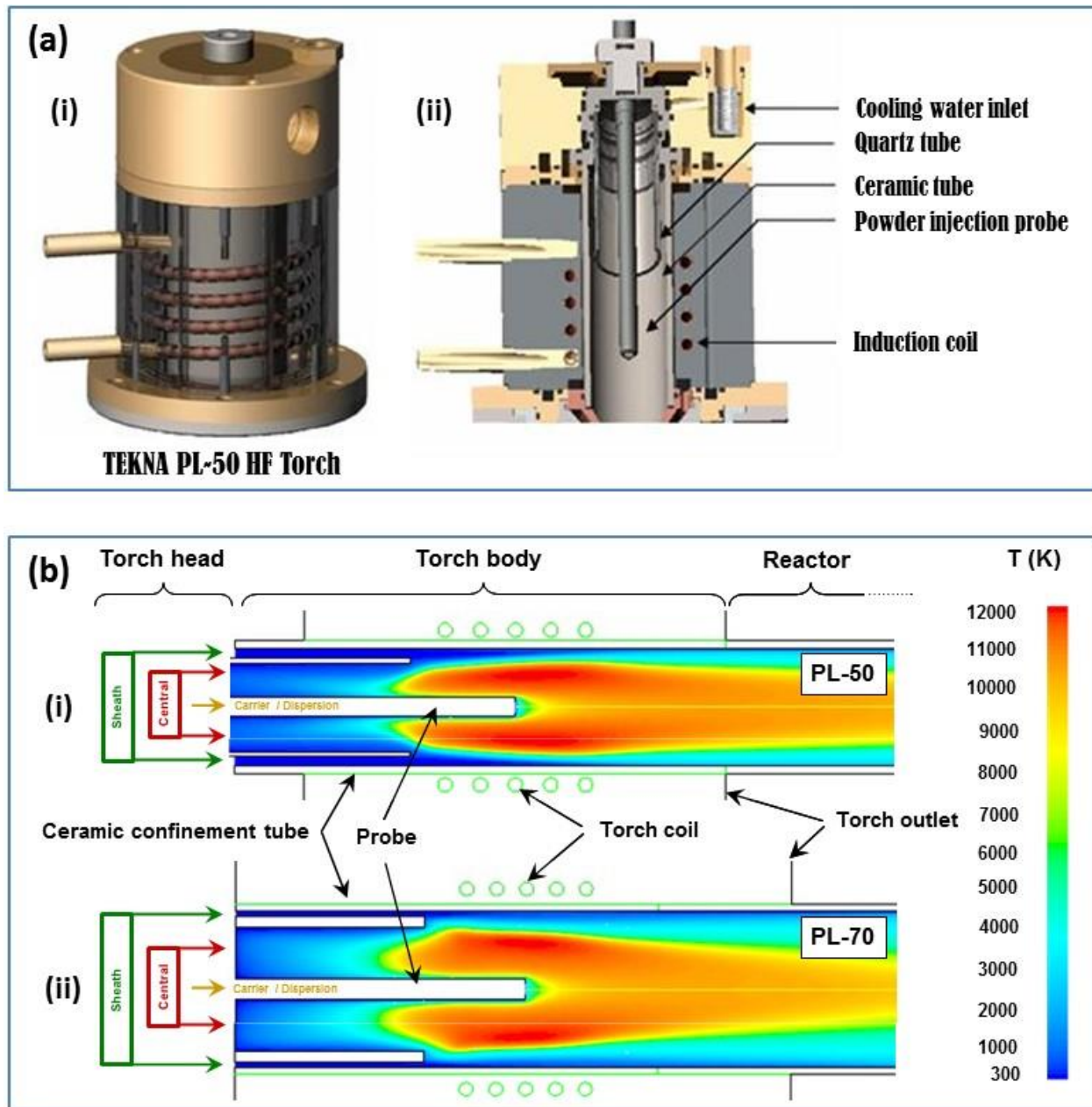
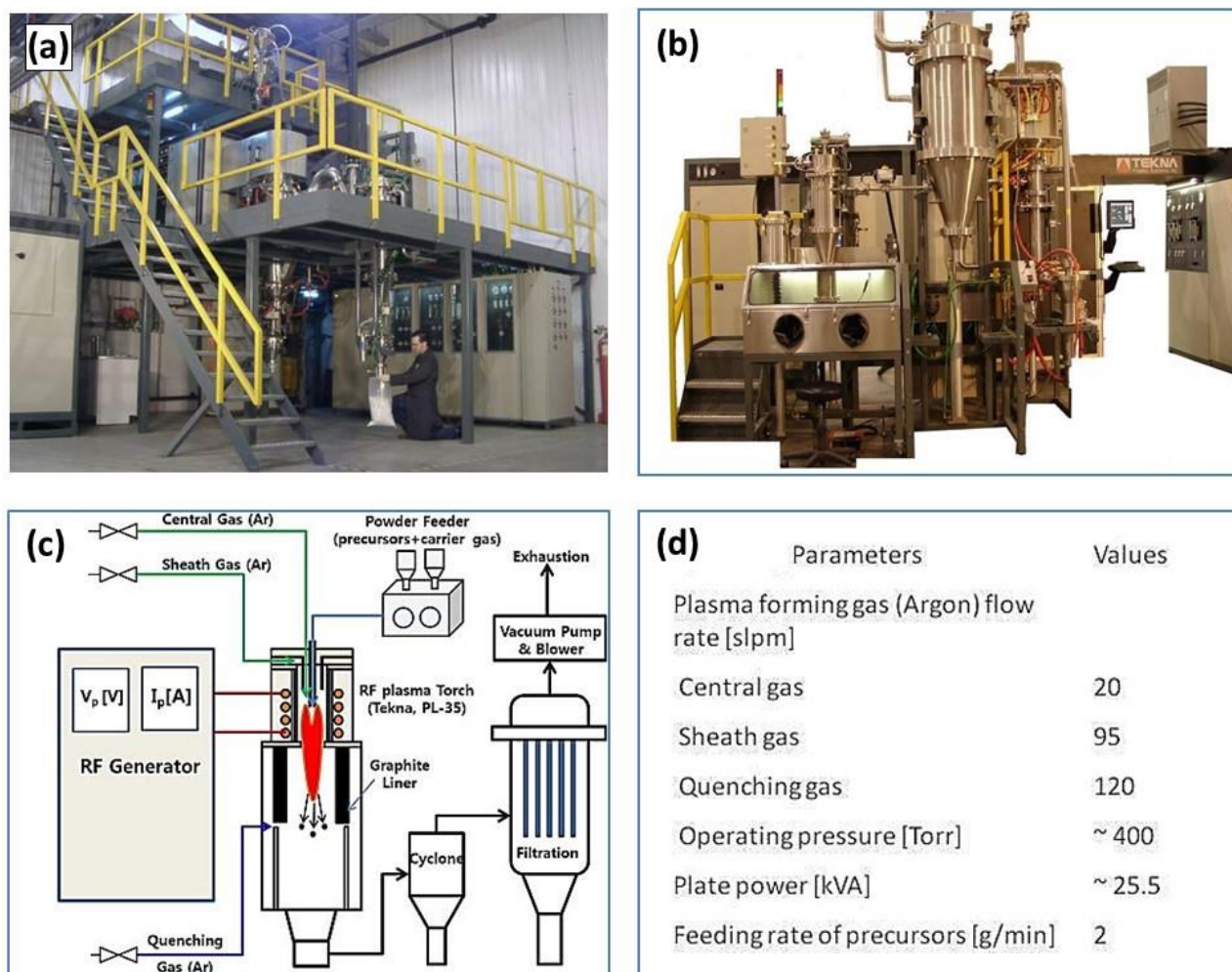


Figure 10. Characteristics of RF torches manufactured by Tekna Plasma Systems, Inc.; (a) Construction schematics; (i) PL-50 torch body; (ii) the inner workings (ref. 23); (b) Typical thermal profiles [calculated]; (i) PL-50; (ii) PL-70 (ref. 26).

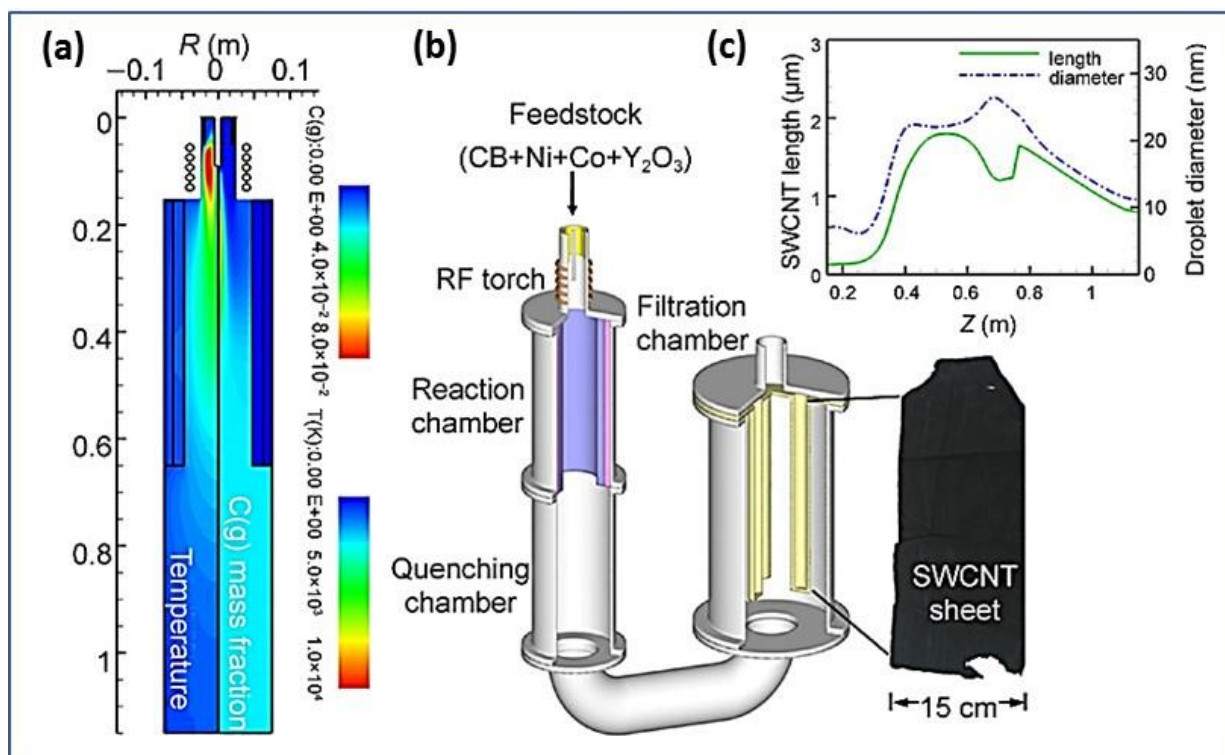


## Radio Frequency Plasma Synthesis of Boron Nitride Nanotubes (BNNTs) for Structural Applications: Part I



**Figure 11.** Tekna Plasma Systems, Inc.; (a) Industrial facility for spheroidization of bulk powder (ref. 5); (b) Induction plasma installation for nanopowders synthesis (inert environment) (ref. 28); (c) Schematic of equipment supporting RF torch operation (ref. 27); (d) Typical settings for a Tekna PL-35 torch (ref. 27).

Figure 12b shows the prototype reactor designed for the mass production of CNTs (ref. 29). The Tekna RF plasma torch has a five-turn induction coil, which is energized by a 40 kW Lepel power supply. Typically, SWNT synthesis is conducted at a fixed plate power of 40 kW, an operating frequency ~3 MHz, and a constant chamber pressure of ~66 kPa. During stable operation, the sheath gas (He) is maintained at a constant flow rate of 120 slpm, the central gas (Ar) is supplied at 25 slpm, and the powder carrier gas (Ar) is injected at 5 slpm. Powder feedstock is delivered axially by the probe at feed rates of 72–120 g/h. Extensive mathematical modeling, validated by enthalpy probe and calorimetric measurements, has permitted the temperature profile and fluid flow in the plasma plume to be characterized (fig. 12a) (refs. 30 and 31).



**Figure 12.** University of Sherbrooke; (a) Mathematical modeling of temperature profile during CNT synthesis; (b) Schematic of apparatus used for RF plasma processing of SWCNT sheets; (c) Typical characteristics of product (ref. 29).

It is worth studying the anatomy of this system in more detail because it provides useful guidelines for the current effort (fig. 13). The reaction chamber is a double-walled cylindrical tube with the primary purpose of providing a suitable environment for the formation and growth of CNTs. The chamber contains interchangeable graphite inserts for flexible control of processing temperature and cooling rate. The quenching chamber comprises a double-walled cylindrical segment, which provides a region for the completion of SWNT growth and for the initiation of secondary chemical reactions. The chamber is equipped with multiple ports for injection of chemical agents for *in-situ* purification or functionalization. The cylindrical filtration chamber contains tubular porous metallic filters, which separate the solid SWNT-containing materials from the residual gases.

This research activity continues and employs a similar Tekna RF plasma torch to that installed in the LaRC facility. The design of the system and the precursors injected also bear a striking resemblance to pioneering Russian work in this arena (ref. 32). A shortcoming of this approach is that the graphite inserts would become a source of contamination during BNNT synthesis. In addition, the tubular filter system limits the process to batch quantities and is not compatible with mass production. However, the process could be readily adapted to the synthesis of BNNTs at LaRC by replacing the reaction and quenching chambers with the very large chamber (fig. 14). The throw distance is very long, and plume length can be controlled by the ambient chamber pressure. The extent of both the hot zone and the cooling zone could potentially be controlled in free flight. In addition, the filter system could be replaced by a cyclone separator to facilitate semi-continuous production.

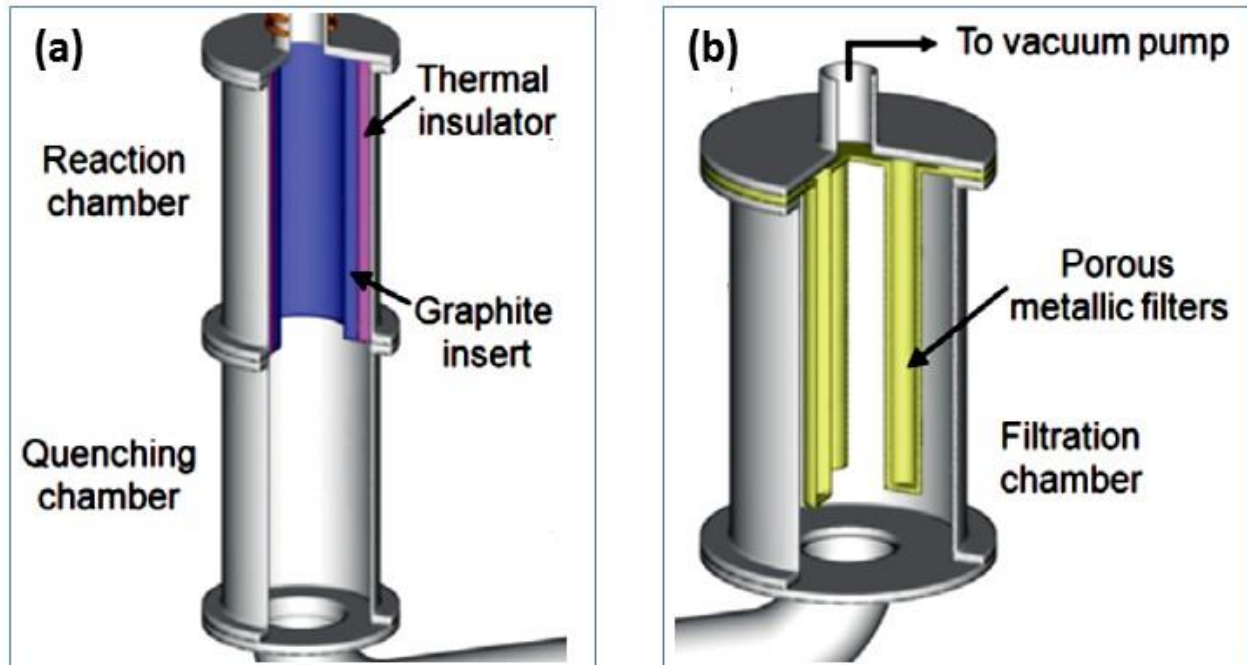


Figure 13. Significant features of University of Sherbrooke apparatus; (a) Construction of synthesis chambers; (b) CNT collection unit geometry (ref. 29).

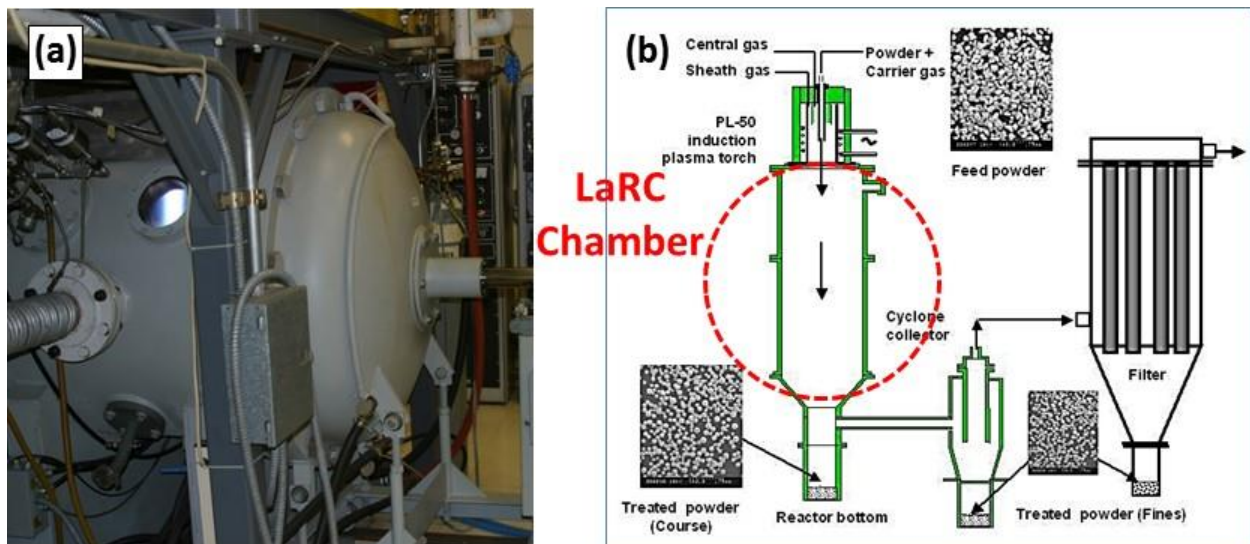


Figure 14. Potential replacement of sequential reaction/quenching chambers; (a) LaRC facility; single 1 m diameter x 1 m long chamber; (b) Tekna facility; dual 0.4 m diameter x 0.5 m long chambers (ref. 5).



## 2.4. RF Plasma-Chemical Synthesis

In the 1980s, the Russian nuclear industry championed RF plasma-chemical synthesis of very fine powders of metallic carbides and nitrides (refs. 24 and 32). The reactions were promoted either inside or outside of the plasma discharge zone, and the reactants were in the solid, liquid, or gas phase. In summarizing the extensive research effort, the processing permutations of significance to the LaRC effort are listed below.

### 2.4.1. Silicon Carbide Nano-powders Produced Inside the Plasma Discharge Zone

The synthesis reaction adopted in this approach involves an equation of the following form:

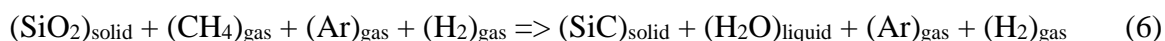


Figure 15 shows a schematic of the RF plasma reactor used to convert a solid metal oxide ( $\text{SiO}_2$ ) into a solid metal carbide ( $\text{SiC}$ ) (ref. 24). The reaction occurred in the presence of reactive gas, such as methane ( $\text{CH}_4$ ), and without evaporation of the precursor powders. The reagents were injected axially ( $\text{SiO}_2 + \text{H}_2$ ) and radially ( $\text{CH}_4 + \text{Ar}$ ) into the torch and the reaction occurred inside the discharge zone. Note that additional  $\text{H}_2$  was introduced into the zone to prevent carbon deposition on the inductor walls. The RF torch operated at a discharge power of 9.2 kW, and  $\text{SiO}_2$  was injected at a rate of 45 g/min. The gas flow rates comprised 1.1 slpm for  $\text{CH}_4$ , 17 slpm for Ar, and a total of 17 slpm for  $\text{H}_2$  (including carrier gas). Upon exiting the nozzle, the end product entered a quenching chamber and was collected in a filtration device. The  $\text{SiC}$  particulate produced was 40–150  $\mu\text{m}$  in diameter and the degree of conversion from  $\text{SiO}$  was approximately 100% using this processing route.

### 2.4.2. Titanium Nitride Nano-powders Produced Outside the Plasma Discharge Zone

The synthesis reaction adopted in this approach involves an equation of the following form:



Figure 16 shows a schematic of the RF plasma reactor used to produce metal carbides and nitrides (including BN) from metal chlorides (ref. 32). In essence, a liquid metal chloride ( $\text{TiCl}_4$ ) was vaporized in the presence of reactive gases such as  $\text{N}_2$  and  $\text{H}_2$  or ammonia ( $\text{NH}_3$ ). The ensuing gas-phase synthesis reaction produced a solid metal nitride and gaseous by-product. Ar was simply the inert plasma forming gas, and the reaction occurred outside the discharge zone. This approach thereby avoided any deposits forming within the plasma gun and allowed for more continuous operation. Only Ar was injected into the torch, and the reagents ( $\text{TiCl}_4 + \text{N}_2 + \text{H}_2$ ) were subsequently introduced radially at the exit nozzle. The conversion reaction occurred between the evaporated liquid and the dissociated gases downstream of the torch. The  $\text{TiN}$  particulate produced was 10–50 nm in diameter, and the degree of conversion from  $\text{TiCl}_4$  was approximately 80% using this processing route.

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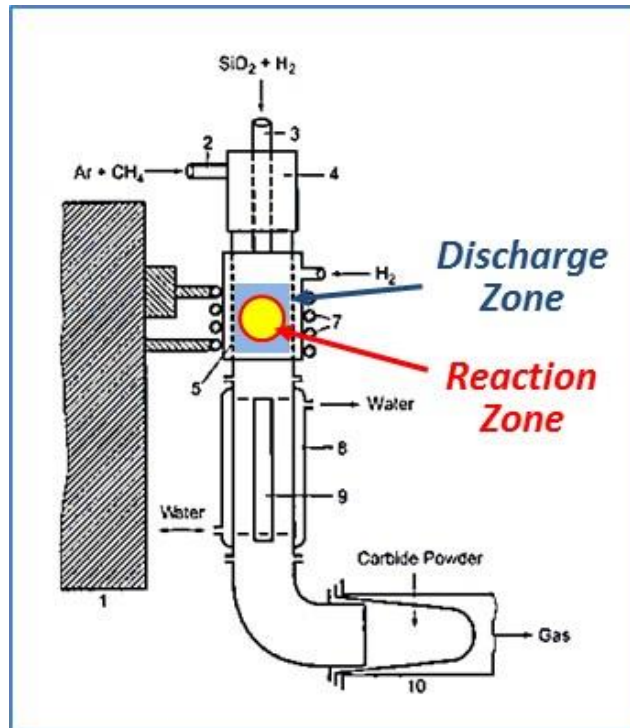


Figure 15. RF plasma process using axial injection of solid and gaseous precursors, with reaction occurring inside the discharge zone (refs. 24, and 32).

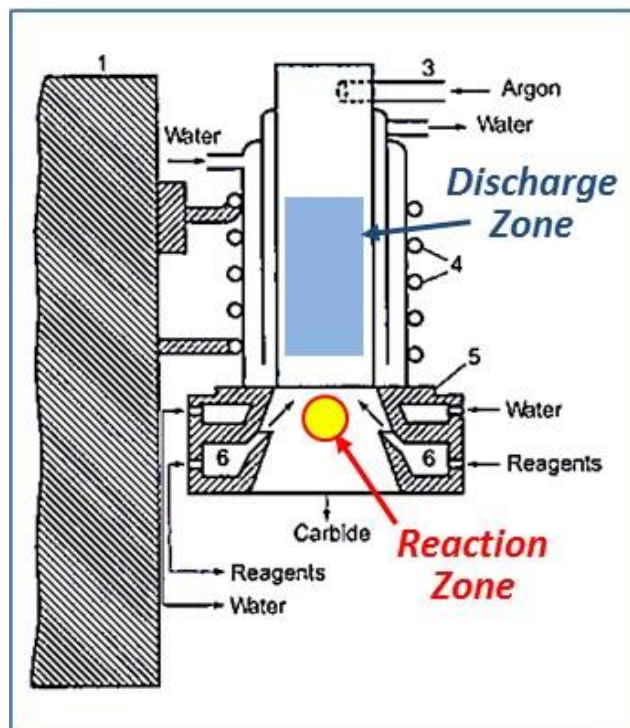


Figure 16. RF plasma process using radial injection of liquid and gaseous precursors, with reaction occurring outside the discharge zone (refs. 24, and 32).

### 3. Proposed LaRC RFPS Approach

#### 3.1. Processing Philosophy

The phase diagram for boron nitride is of particular relevance to the allotropic transformation (thermal plasma) approach. Complete versions have been compiled for pure carbon and pure boron, but only partial versions are currently available for BN (fig. 17) (refs. 11, 34, and 35). It is recognized that the extreme pressures cited in these studies are not necessarily compatible with an atmospheric RF plasma spray system. However, establishing pressure-temperature ( $P$  vs.  $T$ ) diagrams indicating the phase field where NT formation is prevalent in the appropriate pressure regime could be beneficial. Computational modeling will undoubtedly aid in reducing the scope of the experimental matrix by tightening the boundaries (refs. 30 and 31). Process simulation will allow correlation of control settings with  $P$  and  $T$ , and define the relationship with product quality. The objective would be to identify the  $P$  vs.  $T$  regime in which high-purity, low-defect, and small-diameter BNNTs are produced. The development of such a thermodynamic phase diagram would be an important consideration for any proposed research.

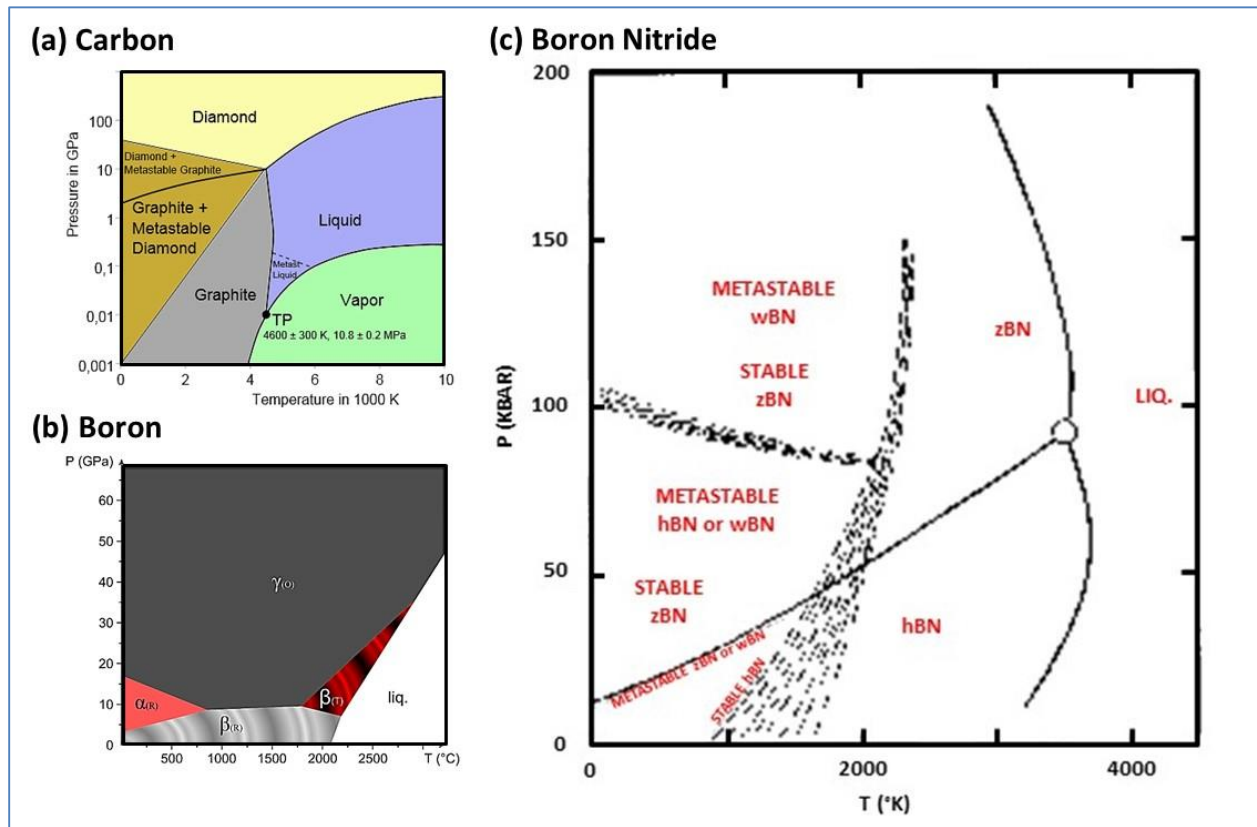


Figure 17. Pressure vs. Temperature phase diagrams; (a) pure carbon (ref. 34); (b) pure boron (ref. 35); (c) boron nitride (ref. 36).

Previous BNNT processing work has shown that lower temperature processing tends to produce large diameter MWNTs which are laden with defects (ref. 3). It is accepted that effective production of SWNTs requires the combination of very high temperatures with low pressure. Researchers have demonstrated that the higher the growth temperature, the better the reactions necessary for crystallization occur and the fewer the defects (ref. 2). It is also possible to customize the synthesis recipe to promote the formation of BNNTs with a specified crystal structure and morphology. In this work, the critical temperatures for RFPS synthesis of BNNTs are the sublimation point of BN (2973°C) for thermal plasma processing, and the vaporization point of B (3927°C) for plasma-chemical processing (refs. 13 and 35). Very high-temperature/partial-pressure RF plasma techniques have already been used to produce high-purity, single-walled CNTs (ref. 29). However, it is recognized that there is a disadvantage to this synthesis approach. The nanotube length is typically rather short due to the spraying action characteristic of the process (ref. 33). In this effort, it is anticipated that what the final product may lack in NT length will be more than compensated for by the purity, consistency, and lack of defects.

### **3.2. Characteristics of the Facility**

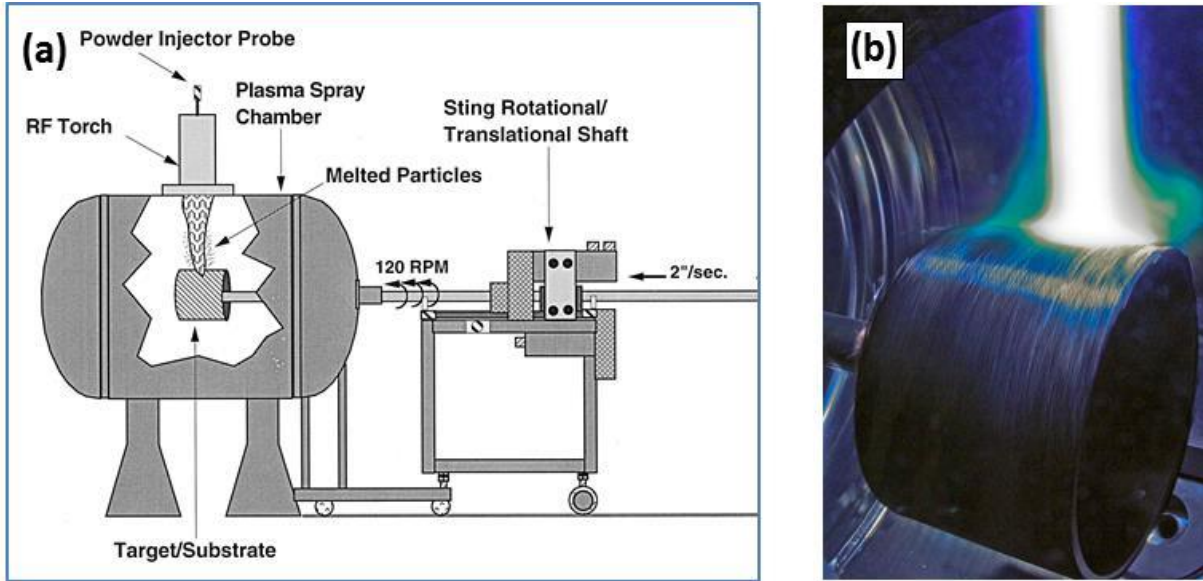
The LaRC RFPS facility was originally procured to process high-melting point, highly-reactive metallic materials into thin gages and/or fiber-reinforced composites. More recent applications of RF plasma spray processing has included;

- thin-gage, difficult-to-process materials:  $\gamma$ -titanium aluminide foils for thermal protection system applications on launch vehicles (ref. 37)
- metal coated glass fabric: porous fiber/metal preforms for hybrid laminate materials (refs. 38 and 39)
- metal coated textiles: metallic filigrees of copper for lightning protection
- multi-metal coated carbon fabric: functional layers of tantalum, copper, and titanium for radiation protection (Z-shielding) (ref. 40)

Figure 18a illustrates the main features of the RFPS facility at NASA LaRC. The apparatus consists of a horizontally-mounted, water-cooled cylindrical chamber with a water-cooled, rotating/translating mandrel (fig. 18b). The static RF torch is vertically-mounted on the 1-meter diameter by 1-meter long chamber. The system is driven by a 240 kVA Lepel generator, with a maximum output of 100 kW and tunable oscillator frequencies of 150–450 kHz. The system consists of five independent mass flow meters which allow up to 850 slpm of inlet gases. Powder feed rates can be carefully controlled between 1 and 100 g/min, and typical particle size is 75–125  $\mu\text{m}$ . Typically, a mixture of Ar and He is used as a plasma-forming gas for generating temperatures up to 3000°C. A partial pressure of  $\text{H}_2$  is introduced (up to 4% by volume) in order to create much higher plasma temperatures. The operating parameter ranges for the RFPS facility are;

- low pressure = 7–100 kPa
- low velocity = 10–100 m/s
- extended spray distance = 150–600 mm
- long residence time = 10–25 ms

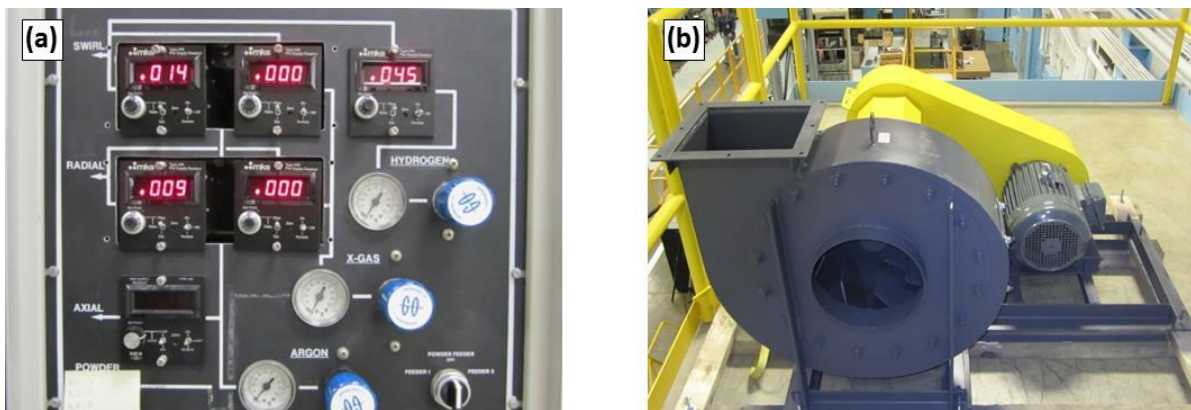
## Radio Frequency Plasma Synthesis of Boron Nitride Nanotubes (BNNTs) for Structural Applications: Part I



**Figure 18.** Radio frequency plasma spray facility located at NASA LaRC; (a) Features of the processing unit; (b) Deposition on fabric-wrapped mandrel.

### 3.3. Facility Modifications for BNNT Synthesis

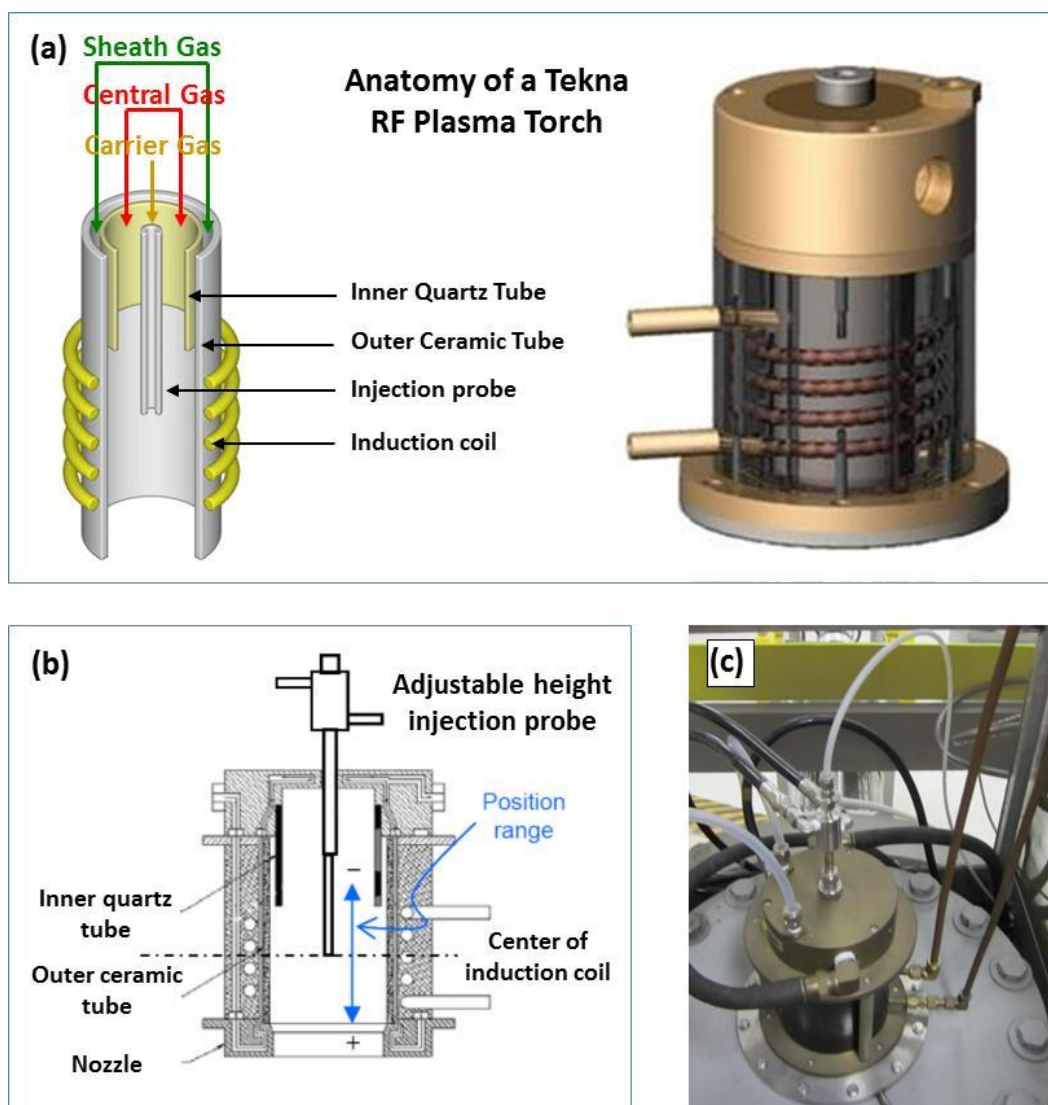
In order to transition from an old plasma gun designed for the spraying of metals, several upgrades to the LaRC RFPS facility were deemed necessary. The first was to replace the mass flow controllers for the gaseous precursors in order to increase the flow rate capability (fig. 19a). Second, the ability to contain potentially hazardous products using a hydrostatic precipitator was paramount for operational safety (fig. 19b). The improved gas management system will allow for careful control of an increased volume of inlet gases. An upgrade of the exhaust filtering system was considered to be critical. The new high-volume exhaust system, including hydrostatic precipitator, will permit effective handling of any toxic outlet gases and by-products. Third, a new plasma torch, manufactured by Tekna, was installed (fig. 20). In contrast to the old torch manufactured by (now defunct) Praxair/TAFA Corp., this provides ready access to spare parts and technical support from an active vendor.



**Figure 19.** Gas control in LaRC RFPS facility; (a) Inlet gases; (b) Outlet gases.



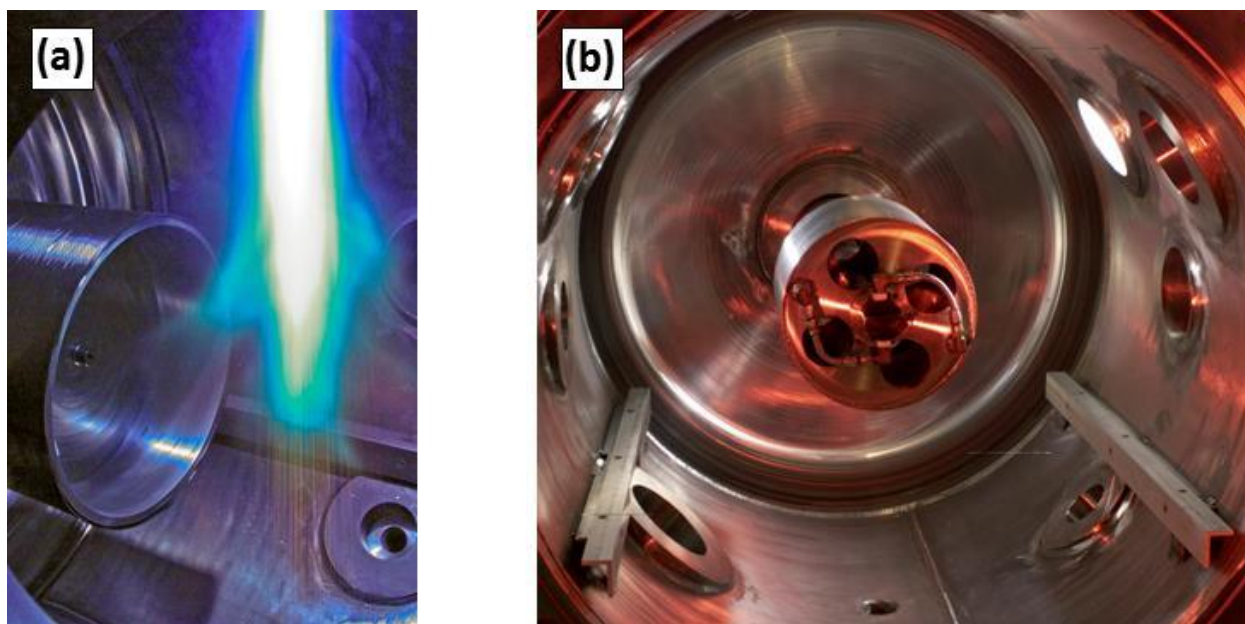
# Radio Frequency Plasma Synthesis of Boron Nitride Nanotubes (BNNTs) for Structural Applications: Part I



**Figure 20. Tekna RF plasma torch; (a) Anatomy of a typical torch (refs. 23, and 30); (b) Adjustable height axial injection probe (ref. 19); (c) Modular installation of PL-70 torch at LaRC.**

Figure 20a illustrates the anatomy of a typical RF torch manufactured by Tekna Plasma Systems, Inc. The torch assembly consists of three basic components; the induction coil, the plasma confinement tube(s), and the gas distribution head. The LaRC PL-70 has a 7-turn coil and can be operated up to an induction power of 100 kW. The outer and inner confinement tubes are fabricated from silicon nitride and quartz, respectively. The gas distributor is responsible for the injection of different gas streams into the discharge zone. The outermost sheath gas is introduced in a manner that produces a helical or straight flow and is responsible for protecting the confinement tube. The central gas is introduced in such manner as to cause a swirling action and is responsible for forming the plasma. The carrier gas is introduced via an injection probe located at the center of the torch head. Multiple choices for both gas composition and flow rates allow for a great deal of flexibility and permit a broad spectrum of processing conditions. The probe allows solid, liquid, or gaseous precursors to be introduced axially with the carrier gas.

The height of the injector within the discharge zone is readily adjustable (fig. 20b). The torch design is modular so that the installation can be removed for periodic maintenance (fig. 20c). In addition, retraction of the mandrel apparatus will facilitate free-flight plasma processing of precursors by increasing the residence time in the hot zone (fig. 21a). Plus, auxiliary access ports through the chamber wall are available for collection/separation/fractionation of free-flight sprayed product (fig. 21b). One objective will be to devise an effective means of isolating BNNTs from the by-products, and also dividing them based on architecture. Some consideration of the devices available for capturing fine particulate is pertinent for the continuous production of BNNTs. These may include cyclonic and electrostatic separators or combinations thereof, which have been successfully applied to nanoparticle collection (fig. 22) (refs. 41 and 42). For example, an industrial unit based on the concept shown in figure 22a, has a processing capacity of 20-40 kg/h for ultrafine, spheroidized powders (ref. 5).



**Figure 21. Important features of LaRC RFPS facility; (a) Mandrel retraction to permit free-flight synthesis; (b) Chamber interior showing auxiliary access ports.**

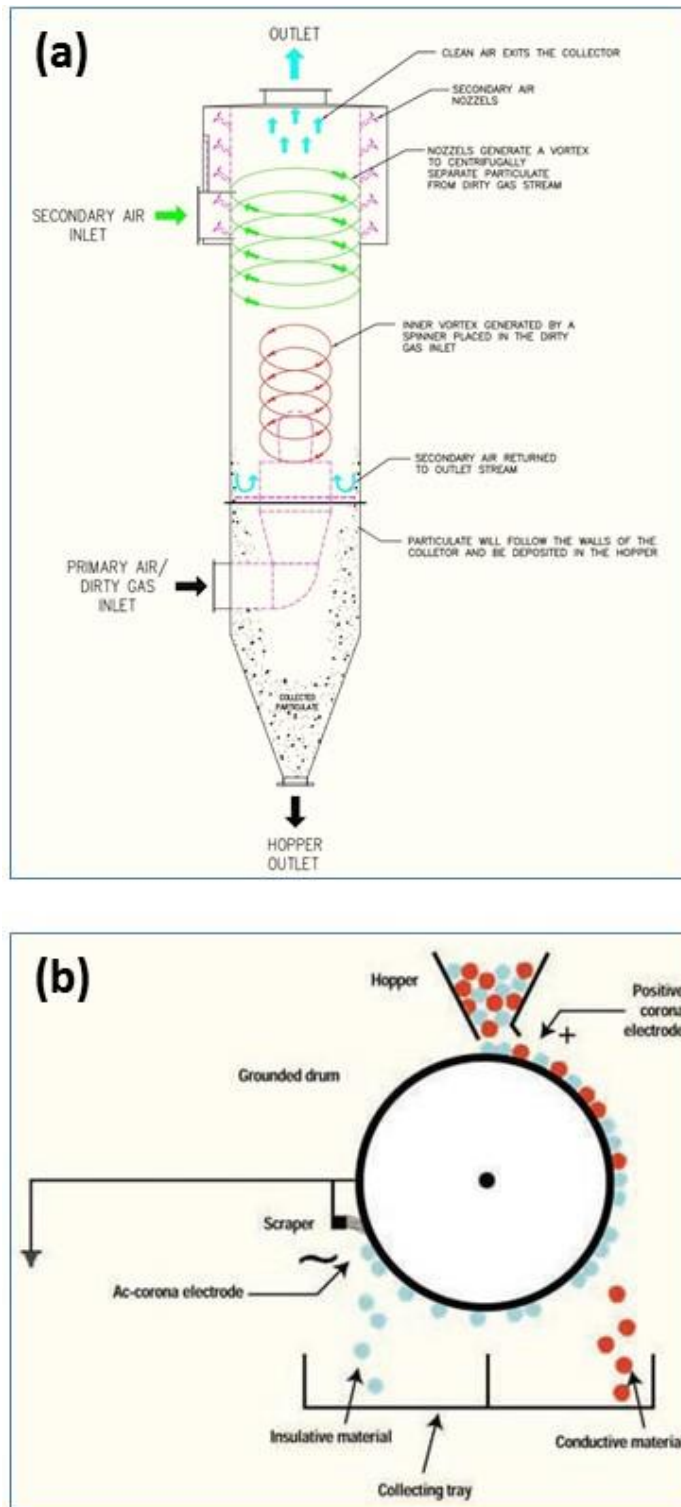
### **3.4. Experimental Methodology**

#### **3.4.1. Thermal Plasma Processing**

The projected processing path involves decomposition of h-BN powders to form dissociated gases already with the correct stoichiometry, followed by recombination to form BNNTs. The simplest route is to take a BN precursor and induce an allotropic transformation using high-temperature plasma at a specified pressure (ref. 36). The BN needs to be vaporized and then encouraged to form BNNTs on cooling, hopefully in the absence of a catalyst. If successful, this would yield a product of extreme cleanliness because of the lack of reactive species and the deliberate introduction of contaminants. In this case, the projected synthesis reaction will follow an equation of the form below:



# Radio Frequency Plasma Synthesis of Boron Nitride Nanotubes (BNNTs) for Structural Applications: Part I

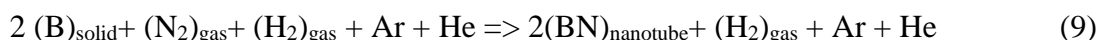


**Figure 22.** Candidate continuous collection devices for LaRC RFPS facility; (a) High volume cyclone separation concept (ref. 41); (b) Principle behind high volume electrostatic drum separators (ref. 42).

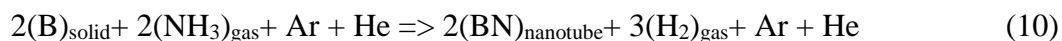


### 3.4.2. Plasma-Chemical Processing

The projected processing path involves vaporization of B powders, combination with dissociated nitrogen gas with 1:1 stoichiometry, followed by an *in-situ* chemical reaction to form BNNTs. The more complicated route is to take a B precursor and combine it with reactive species outside of the discharge zone. This approach may produce a more reliable product in a more controlled manner. Dwell times, temperatures, and gas compositions can be monitored and adjusted for maximum yield, consistency, or aspect ratio. It is possible to use a suspension probe such that the metallic powder precursor can be introduced in fluid form, i.e. very fine particulate suspended in a medium. The downside of this methodology is the possibility of organic contamination. In this case, the projected synthesis reaction will follow equations of the form below:



or



### 3.4.3. Manageable Experimental Matrix

The combination of implementing two fundamentally different approaches and having many permutations for the processing parameters dictates the formulation of a manageable test plan. The underlying experiment is to vary the plasma temperature and the operating pressure. The many equipment settings governing these process variables include, but may not be restricted to the following:

- Feedstock = high-purity, 30-50  $\mu\text{m}$  diameter B or h-BN powders
- Induction power and frequency
- Gas flow rates
- Carrier / Central / Sheath gas balance
- Argon (Ar) / Helium (He) / Hydrogen ( $H_2$ ) balance
- Substitution of Nitrogen ( $N_2$ )
- Injection probe position (inside vs. outside discharge zone)

## 3.5. Projected Outcome

In the prior Russian work, most plasma conversion processes were conducted outside the discharge zone, so that only the inert, plasma-forming gas was inductively heated. The advantage to introducing reactants downstream of the plasma torch was that the deposition of conductive products within the discharge chamber was avoided. Experience revealed that such deposits progressively prevented effective coupling of the RF inductor with the reactive precursors and inhibited plasma formation. In this case, neither B nor BN are classified as conductive products, which does create the opportunity for plasma synthesis inside the discharge zone. However, any deposits within the chamber will impact torch performance, rendering this

## **Radio Frequency Plasma Synthesis of Boron Nitride Nanotubes (BNNTs) for Structural Applications: Part I**

approach less attractive. In addition, many of the plasma-chemical synthesis techniques are not very appealing because dangerous by-products, such as hot hydrochloric acid, tend to be involved. Consequently, if thermal plasma synthesis alone is effective either inside or outside the discharge zone, then proceedings will be greatly simplified. RFPS technology readily lends itself to very high-processing temperatures and high-purity product. The objective of designed experiments will be to identify the parameters promoting the synthesis of low-defect, small-diameter BNNTs. In light of historical processing difficulties, production of large quantities of high-purity BNNTs with any architecture or aspect ratio may be considered a bonus.

## 4. Concluding Remarks

The projected advantages of using the LaRC RFPS facility for the synthesis of large quantities of high-purity BNNTs may be summarized as follows:

Problem: Synthesis of high-quality BNNTs requires much higher temperatures than CNTs ( $> 4,000^{\circ}\text{C}$ ).

Solution: Use inductively-coupled (RF) plasma which has a temperature capability of  $\sim 12,000^{\circ}\text{C}$ .

Problem: Incumbent arc discharge processes are low-volume, high-velocity processes; radial powder feed, short dwell times.

Solution: RF plasma is a high-volume, low-velocity process; axial powder feed, long residence time (+ adjustable plume length and powder injector height).

Problem: Incumbent methods are batch processes (not compatible with mass production).

Solution: RFPS is a semi-continuous process which is readily scalable.

Problem: Impurities result from consumable electrodes/targets and catalysts.

Solution: RF plasma processing uses no electrodes or targets (and may avoid catalyst usage).

Problem: Handling of end product can be hazardous, e.g. pyrophoric, asbestosis.

Solution: Entire RF plasma process occurs within a self-contained, inert gas environment.

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## Appendix A.

Prior to the publication of this White Paper, details concerning work being performed at the National Research Council - Canada (NRC-C) emerged (ref. 43). Evidently, this effort is an extension of an earlier campaign to mass produce CNTs (fig. A-1), accompanied by extensive modeling of RF plasma synthesis of NTs (refs. 44, 45 and 46). The current activity involves the allotropic transformation of h-BN powder into high quality BNNTs in the presence of a hydrogen catalyst. Although only a partial processing recipe is accessible, it is apparent that the approach is very successful at producing large quantities. A 60kW RF induction plasma torch generates plasma temperatures  $> 7,700^{\circ}\text{C}$ , causing dissociation of the reactants. Subsequently, a controlled thermal gradient between  $\sim 3,700^{\circ}\text{C}$  and  $\sim 2000^{\circ}\text{C}$  causes BNNT growth in a reaction chamber. The RF torch is coupled to a  $\sim 1$  m long by  $\sim 20$  cm diameter, ceramic-lined reactor maintained at  $\sim 720$  torr. Best results are obtained when the plasma-forming gas is a ternary mixture of Ar,  $\text{N}_2$ , and  $\text{H}_2$ , and the powder feedstock is pure h-BN, injected at a rate of 0.5-1.0 g/min.

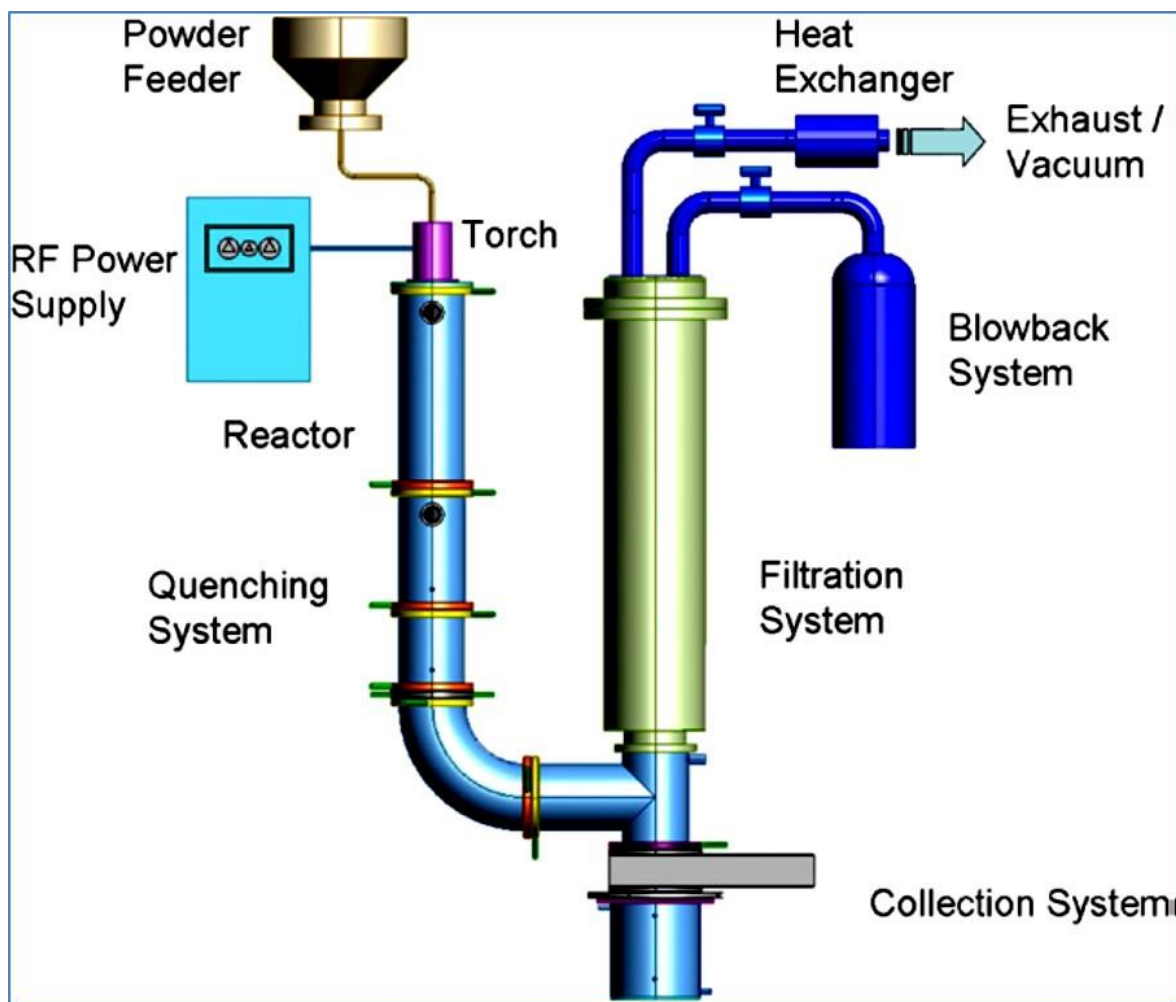


Figure A-1. Prototype RF plasma reactor developed for synthesis of CNTs (ref. 45).

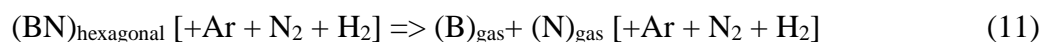


## Radio Frequency Plasma Synthesis of Boron Nitride Nanotubes (BNNTs) for Structural Applications: Part I

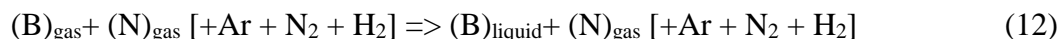
The NRC-C group subscribes to the “root-growth model” for BNNT formation in the current work (ref. 47). The sequence of BNNT growth during the RF processing is cited as consisting of the following:

- Vaporization of BN source
- Decomposition of BN vapors into boron and nitrogen
- Formation of nano-sized boron droplets
- Reaction between boron nanoparticles and nitrogen
- Growth of BNNT from boron nanoparticles

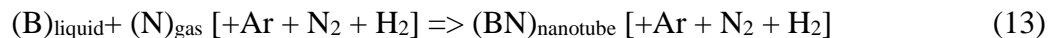
Based on this proposed sequence of events, the synthesis reaction involves equations of the following form:



and



and



A mixture of “candy cotton-, fibril-, and cloth-like” material was produced at a rate of 10–20 g/h, and the wispy material could be readily finger-twisted into > 20 cm long yarns (ref. 43). Analysis revealed that all of the materials consisted of few-walled BNNTs (< 10 nm in diameter). However, the product purity via the method described was ~65%, with the balance comprising ~25% BN-derivatives and ~10% amorphous B particles. Consequently, there are opportunities for LaRC activities to improve upon the NRC-C effort by using process diagnostics, statistically designed experiments, and even to develop a phase diagram. The emphasis of synthesis activities will shift toward adjusting these ratios and maximizing the purity of the end product. The incumbent method may employ a friable liner for the narrow reaction chamber which may be a source of contamination, and free-flight synthesis in a wide-open chamber may be a benefit. An additional LaRC objective may be the RFPS deposition of metals on to NRC-generated BNNT material, followed by VARTM processing, in order to produce hybrid laminate composites (refs. 37 and 38). However, there is considerable work remaining if the mechanical properties of the end product are even going to approach theoretical values (table A-1) (refs. 43, 48, and 49). Lastly, research on collection devices for *in-situ* nanotube separation and alignment may prove most useful in this endeavor, e.g. the utilization of cyclonic, electrostatic and/or spooling separator technologies (refs. 40, 41, and 50).

Radio Frequency Plasma Synthesis of Boron Nitride Nanotubes  
(BNNTs) for Structural Applications: Part I

**Table A-1. Comparison of mechanical properties of boron nitride- and carbon-based materials (refs. 43, 48, and 49).**

Material	Tensile Strength Gpa (Msi)	Young's Modulus Gpa (Msi)
Carbon Fiber	5.6 (0.8)	530 (76.9)
Carbon Nanotube <sup>+</sup>	150 (21.8)	900 (130)
<i>Carbon Nanotube Yarn*</i>	<i>9 (1.3)</i>	<i>350 (50.8)</i>
Boron Nitride Nanotube <sup>+</sup>	33 (4.8)	1200 (174)
<i>Boron Nitride Nanotube Yarn**</i>	<i>9.6 (1.4)</i>	<i>500 (72.5)</i>
Graphene	130 (18.9)	1000 (145)
Diamond	60 (8.7)	1200 (174)

Theoretical properties of BNNTs compared with carbon-based materials (\* pristine, single-walled) (ref. 48).  
*MEASURED; Twisted NT bundles; \* 7  $\mu$ m dia. x 20 mm long (ref. 49); \*\* 150  $\mu$ m dia. x 22 cm long (ref. 43).*

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